



- Hypothesizing
- Analyzing and interpreting

Method 1

At the time that Rutherford was performing his experiments, physicists knew that the diameter of the entire atom was about 10^{-10} m.

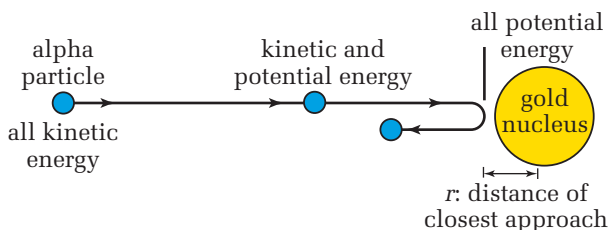
- Calculate the cross-sectional area of the atom, assuming that its diameter is 10^{-10} m.

Rutherford's students observed that about 1 in every 20 000 alpha particles scattered backward from the foil. If they were all headed toward the atom but only 1 in 20 000 was headed directly toward the nucleus, what must be the cross-sectional area of the nucleus?

- Calculate the cross-sectional area of the nucleus based on the above information.
- Using your cross-sectional area of the nucleus, calculate the diameter of the nucleus.

Method 2

Make a second estimate of the size of the nucleus based on the conservation of mechanical energy of the alpha particle. As shown in the diagram, at a large distance from the nucleus, the energy of the alpha particle is all kinetic energy. As it approaches the nucleus, its kinetic energy is converted into electric potential energy. When all of its kinetic energy is converted into electric potential energy, the alpha particle will stop. At this point, called the "distance of closest approach," the repulsive Coulomb forces will drive the alpha particle



directly backward. If the alpha particle penetrated the nucleus, it would be trapped and would not scatter backward.

- The equation below states that the kinetic energy of the alpha particle at a large distance from the nucleus is equal to the electric potential energy of the alpha particle at the distance of closest approach. Substitute into the equality the mathematical expressions for kinetic energy and electric potential energy between two point charges a distance, r , apart.

$$E_k \text{ (very far from nucleus)} \\ = E_Q \text{ (distance of closest approach)}$$

- The mass of an alpha particle is about 6.6×10^{-27} kg and those that Rutherford used had an initial velocity of 1.5×10^7 m/s. Calculate the kinetic energy of the alpha particle.
- An alpha particle has 2 positive charges and a gold nucleus has 79 positive charges. Using the magnitude of one elementary charge (1.6×10^{-19} C), calculate the magnitude of the charges needed for the determination of the electric potential energy.
- Substitute all of the known values into the equation above. You will find that r is the only unknown variable. Solve the equation for r , the distance of closest approach.

Analyze and Conclude

1. Comment on the validity of each of the two methods. What types of errors might affect the results?
2. How well do your two methods agree?
3. The accepted size of an average nucleus is in the order of magnitude of 10^{-14} m. How well do your calculations agree with the accepted value?

The Bohr Model of the Atom

Rutherford's model of the atom was based on solid experimental data, but it had one nagging problem that he did not address.

According to classical electromagnetism, an accelerating charge should radiate electromagnetic waves and lose energy. If electrons are orbiting around a nucleus, then they are accelerating and they should be radiating electromagnetic waves. If the electrons lost energy through radiation, they would spiral into the nucleus.

According to Rutherford's model, electrons remain permanently in orbit.

Niels Henrik David Bohr (1885–1962) addressed the problem of electrons that do not obey classical electromagnetic theory. Bohr was born and educated in Denmark, and in 1912, went to study in Rutherford's laboratory in Manchester. (Rutherford said of Bohr, "This young Dane is the most intelligent chap I've ever met.") Convinced that Rutherford was on the right track with the nuclear atom, Bohr returned home to Copenhagen, where he continued his search for an explanation for the inconsistency of the nuclear atom with classical theory.

Bohr was very aware of the recent publications of Planck and Einstein on blackbody radiation and the photoelectric effect, and that these phenomena did not appear to obey the laws of classical physics. He realized that some phenomena that are unobservable on the macroscopic level become apparent on the level of the atom. Thus, he did not hesitate to propose characteristics for the atom that appeared to contradict classical laws.

Bohr had another, very significant piece of evidence available to him — atomic spectra. When Kirchhoff defined blackbodies, he was studying very low-pressure gases in gas discharge tubes. Kirchhoff discovered that when gases of individual elements were sealed in gas discharge tubes and bombarded with "cathode rays," each element produced a unique spectrum of light. The spectrum of hydrogen is shown in Figure 12.18.

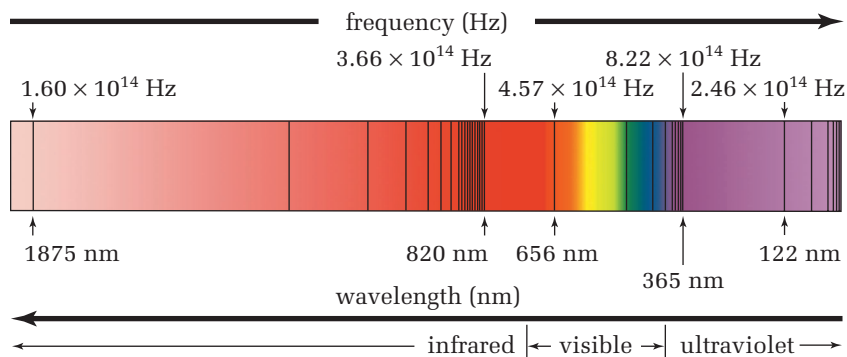


Figure 12.18 When bombarded by high-energy electrons, hydrogen atoms emit a very precise set of frequencies of electromagnetic radiation, extending from the infrared region, through the visible region, and well into the ultraviolet region of the spectrum.

Since emission spectra did not have an immediately obvious pattern, Bohr thought them too complex to be useful. However, a friend who had studied spectroscopy directed Bohr to a pattern that had been determined in 1885 by Swiss secondary school teacher Johann Jakob Balmer (1825–1898). Balmer had studied the visible range of the hydrogen spectrum and found an empirical expression that could produce the wavelength of any line in that region of the spectrum. Balmer's formula is given below. Remember that empirical equations are developed from experimental data and are not associated with any theory. Balmer could not explain why his formula had the form that it did. He could demonstrate only that it worked.

$$\frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{n^2} \right], \text{ where } n = 3, 4, 5, \dots \text{ and}$$

$$R = 1.097\,373\,15 \times 10^7 \text{ m}^{-1}$$

The spectral lines of hydrogen that lie in the visible range are now known as the **Balmer series**. As spectroscopists developed methods to observe lines in the infrared and ultraviolet regions of the spectrum, they found more series of lines. Swedish physicist Johannes Robert Rydberg (1854–1919) modified Balmer's formula, as shown below, to incorporate all possible lines in the hydrogen spectrum. The constant R is known as the **Rydberg constant**.

$$\frac{1}{\lambda} = R \left[\frac{1}{m^2} - \frac{1}{n^2} \right], \text{ where } m \text{ and } n \text{ are integers; } 1, 2, 3, 4, \dots$$

$$\text{and } n > m$$

Bohr Postulates

When Bohr saw these mathematical patterns, he said, “As soon as I saw Balmer's formula, the whole thing was immediately clear to me.” Bohr was ready to develop his model of the atom. Bohr's model, illustrated in Figure 12.19, was based on the following postulates.

- Electrons exist in circular orbits, much like planetary orbits. However, the central force that holds them in orbit is the electrostatic force between the positive nucleus and the negative charge on the electrons, rather than a gravitational force.
- Electrons can exist only in a series of “allowed” orbits. Electrons, much like planets, have different amounts of total energy (kinetic plus potential) in each orbit, so these orbits can also be described as “energy levels.” Since only certain orbits are allowed, then only certain energy levels are allowed, meaning that the energy of electrons in atoms is quantized.
- Contrary to classical theory, while an electron remains in one orbit, it does not radiate energy.
- Electrons can “jump” between orbits, or energy levels, by absorbing or emitting an amount of energy that is equal to the *difference* in the energy levels.

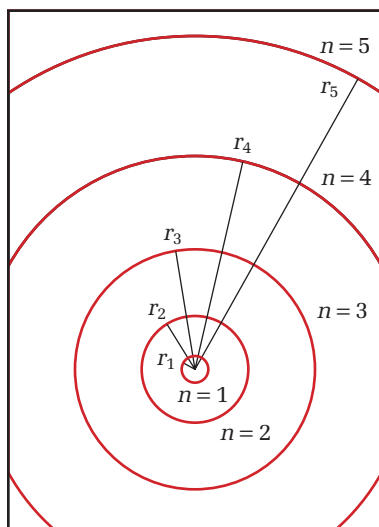


Figure 12.19 According to Bohr's model of the atom, electrons can exist in specific, allowed energy levels and can jump from one level to another by absorbing or emitting energy.

Johann Balmer's life was a contrast to that of most other contributors to the theory of the atom. Balmer taught mathematics in a secondary school for girls and lectured at the University of Basel in Switzerland. He published only two scientific papers in his career, one when he was 60 years old and one when he was 72. Balmer died 15 years before Niels Bohr provided an explanation for Balmer's now famous formula for the emission spectrum of hydrogen.

Electrons can “jump” to higher energy levels by absorbing thermal energy (collision with an energetic atom or molecule), by bombardment with an energetic electron (as in gas discharge tubes), or by absorbing photons of radiant energy with energies that exactly match the difference in energy levels of the electrons in the atom. Likewise, electrons can “drop” to a lower energy level by emitting a photon that has an energy equal to the *difference* between the energy levels. Since the energy of a photon is directly related to the frequency of the electromagnetic waves, you could express this relationship between energy levels and photons as follows.

$$|E_f - E_i| = hf$$

E_f is the energy of the final energy level, E_i is the energy of the initial energy level, and hf is the photon energy. This concept gives meaning to the “2” and the “ n ” in Balmer’s formula, because the “2” represents the second energy level and “ n ” is any energy level above the second one. In Rydberg’s more general formula, m is the final energy level, which can be any level. Likewise, n is the initial level and must therefore be higher than the final level.

To find the exact energies of these “allowed energy levels,” Bohr had to determine exactly what property of the electron was quantized. An important clue comes from the units of Planck’s constant — joule · seconds. First, simplify joules to base units.

$$\text{J} \cdot \text{s} = \text{N} \cdot \text{m} \cdot \text{s} = \frac{\text{kg} \cdot \text{m}}{\text{s}^2} \cdot \text{m} \cdot \text{s} = \text{kg} \cdot \frac{\text{m}}{\text{s}} \cdot \text{m}$$

The final units, $\text{kg} \cdot \frac{\text{m}}{\text{s}} \cdot \text{m}$, are the units for the quantities of mass, speed, and distance, or mvd . At one time in physics, this combination was called “action.” In fact, Planck called his constant, h , the “quantum of action.” If you apply these quantities to the electron in an orbit of radius r , you will get $m_e v_n 2\pi r$, where $2\pi r$ is the distance that the electron travels during one orbit around the nucleus. If this value is quantized, you would have the following.

$$2\pi m_e v_n r_n = nh$$

You might recognize the expression $m_e v_n r_n$ as the angular momentum of the electron in the n^{th} orbit. Following a similar logic, Bohr proposed that the angular momentum was quantized and then tested that hypothesis. The angular momentum of the n^{th} orbit can be written as follows.

$$m_e v_n r_n = n \frac{h}{2\pi}$$

You can test the theory by using the equation for the quantized angular momentum to find allowed radii and allowed energies of electrons. Then, you can compare these differences between energy levels to Balmer’s formula and the Rydberg constant. Since you have two unknown quantities, r and v , you will need more relationships to find values for either r or v in terms of known

constants. Because Bohr based his concept on circular orbits, you can use the fact that the electrostatic force between the electron and the nucleus provides the centripetal force that keeps the electron in a circular orbit. The following steps will lead you through the procedure.

Deriving the Bohr Radius

- Write Coulomb's law. $F = k \frac{q_1 q_2}{r^2}$
- Let Z be the number of positive charges in the nucleus. Therefore, Ze is the charge of the nucleus. The charge on an electron is, of course, e . Let r_n be the radius of the n^{th} orbit. Substitute these values into Coulomb's law. $F = k \frac{Ze^2}{r_n^2}$
- Set the coulomb force equal to the centripetal force. $k \frac{Ze^2}{r_n^2} = \frac{m_e v_n^2}{r_n}$
- Multiply both sides by r_n^2 . $kZe^2 = m_e v_n^2 r_n$
- Divide both sides by $m_e v_n^2$. $r_n = \frac{kZe^2}{m_e v_n^2}$
- Write Bohr's condition for quantization of angular momentum. $m_e v_n r_n = n \frac{h}{2\pi}$
- Solve for v_n . $v_n = \frac{nh}{2\pi m_e r_n}$
- Substitute this expression for v_n into the equation for r_n . $r_n = \frac{kZe^2}{m_e \left(\frac{nh}{2\pi m_e r_n} \right)^2}$
- Start the simplification by inverting the fraction in the denominator in brackets and then multiplying by the inverted fraction. $r_n = \frac{kZe^2}{m_e} \cdot \frac{4\pi^2 m_e^2 r_n^2}{n^2 h^2}$
- Divide both sides of the equation by r_n . $1 = \left(\frac{4\pi^2 kZe^2 m_e^2}{m_e n^2 h^2} \right) r_n$
- Invert and multiply by the expression in brackets. $r_n = \frac{n^2 h^2}{4\pi^2 kZe^2 m_e}$

The expression, $\frac{h}{2\pi}$, occurs so frequently in quantum theory that the symbol \hbar is often used in place of $\frac{h}{2\pi}$. The final expression is usually written as follows.

$$r_n = n^2 \frac{\hbar^2}{m_e kZe^2}$$

For the first allowed radius of the electron in a hydrogen atom, $Z = 1$ and $n = 1$. All of the other values in the equation are constants and if you substitute them into the equation and simplify, you will obtain $r_1 = 0.052\,917\,7\,\text{nm}$. This value is known as the **Bohr radius**.

Deriving Allowed Energy Levels

You can use the equation for the radius of the n^{th} orbit of an electron to find the energy for an electron in the n^{th} energy level in an atom as shown in the following steps.

- Write the expression for the total energy (kinetic plus potential) of a charge a distance, r , from another charge.

$$E = \frac{1}{2}mv^2 - k\frac{q_1q_2}{r}$$

- Substitute in the values for an electron at a distance, r_n , from a nucleus.

$$E_n = \frac{1}{2}m_e v_n^2 - k\frac{Ze^2}{r_n}$$

- To eliminate the variable, v , from the equation, go back to the expression you wrote when you set the Coulomb force equal to the centripetal force.

$$k\frac{Ze^2}{r_n^2} = \frac{m_e v^2}{r_n}$$

- Multiply both sides of the expression by $\frac{r_n}{2}$ and simplify.

$$\left(k\frac{Ze^2}{r_n^2}\right)\left(\frac{r_n}{2}\right) = \left(\frac{m_e v^2}{r_n}\right)\left(\frac{r_n}{2}\right)$$

$$\frac{kZe^2}{2r_n} = \frac{1}{2}m_e v_n^2$$

- Substitute this value found in the last step for kinetic energy, $\frac{1}{2}m_e v_n^2$, in the second equation and then simplify.

$$E_n = \frac{kZe^2}{2r_n} - k\frac{Ze^2}{r_n}$$

$$E_n = -\frac{kZe^2}{2r_n}$$

- Substitute the value for r_n into the expression for energy.

$$E_n = -\frac{kZe^2}{2\left(n^2\frac{\hbar^2}{m_e kZe^2}\right)}$$

- To simplify, invert the fraction in the denominator and multiply.

$$E_n = -\frac{kZe^2}{2(n^2)} \cdot \frac{m_e kZe^2}{\hbar^2}$$

$$E_n = -\frac{k^2 e^4 m_e}{2\hbar^2} \cdot \frac{Z^2}{n^2}$$

Once again, you can write a general formula for the total energy of an electron in the n^{th} level of a hydrogen atom ($Z = 1$) by substituting the correct values for the constants. You will discover that

$E_n = -\frac{13.6 \text{ eV}}{n^2}$. The integer, n , is now known as the **principal quantum number**.

Recalling Bohr's hypothesis that the difference in the energy levels would be the energies of the photons emitted from an atom, you can now use this formula to compare Bohr's model of the atom with the observed frequencies of the spectral lines for hydrogen atoms. For example, you should be able to calculate the frequency of the first line in the Balmer series by doing the following.

$$\begin{aligned}
 hf &= E_3 - E_2 \\
 hf &= \frac{-13.6 \text{ eV}}{3^2} - \left(\frac{-13.6 \text{ eV}}{2^2} \right) \\
 hf &= -1.511 \text{ eV} + 3.40 \text{ eV} \\
 hf &= 1.89 \text{ eV} \\
 f &= \left(\frac{1.89 \text{ eV}}{h} \right) \left(\frac{1.6 \times 10^{-19} \text{ J}}{\text{eV}} \right) \\
 f &= \frac{3.0222 \times 10^{-19} \text{ J}}{6.63 \times 10^{-34} \text{ J} \cdot \text{s}} \\
 f &= 4.56 \times 10^{14} \text{ Hz}
 \end{aligned}$$

This value is in excellent agreement with the observed frequency of the first line in the Balmer series. If you performed similar calculations for the other lines in the Balmer series, you would find the same excellent agreement with observations.

Spectroscopists continued to find series of lines that were matched with electrons falling from higher levels of the hydrogen atom down into the first five energy levels. These series are named and illustrated in Figure 12.20.

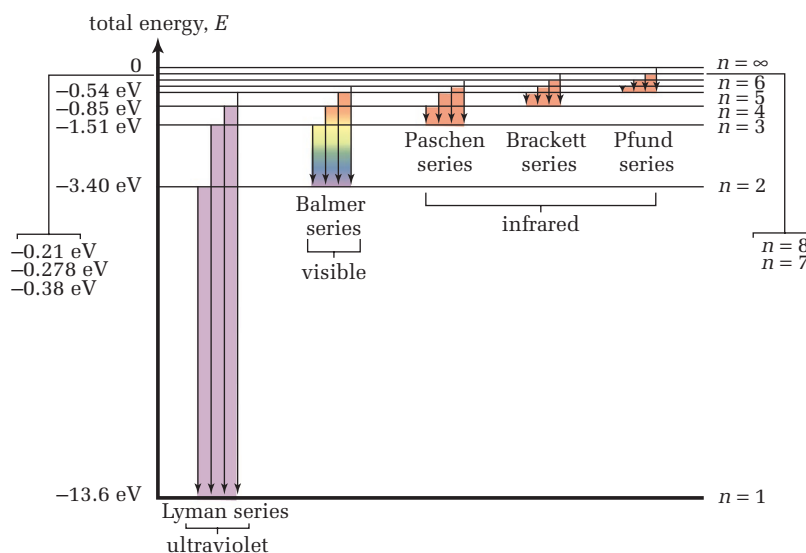


Figure 12.20 Photons from transitions that *end* at the same energy level have energies (and therefore frequencies) that are relatively close together. When inspecting a particular range of frequencies emitted by an element, therefore, an observer would find a set of spectral lines quite close together. Each set of lines is named after the person who observed and described them.

You could perform calculations such as the sample calculation of the frequency of the first line in the Balmer series for any combination of energy levels and find agreement with the corresponding line in the hydrogen spectrum. Bohr's model of the atom was thoroughly tested and was found to be in agreement with most of the data available at the time.

• Conceptual Problems

- Start with the expression $hf = |E_f - E_i|$, then substitute the equation for the energy of the n^{th} level of an electron into E_f and E_i into the first expression. Finally, use the relationship $c = f\lambda$ to derive the following expression.

$$\frac{1}{\lambda} = \left| \frac{2\pi^2 k^2 e^4 m_e Z^2}{h^3 c} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \right|$$

- The equation above would be identical to the Rydberg equation if the combination of constants $\frac{2\pi^2 k^2 e^4 m_e}{h^3 c}$ was equal to the Rydberg constant for hydrogen atoms ($Z = 1$). Calculate the value of the constants and compare your answer with the Rydberg constant. What does this result tell you about Bohr's model of the atom?

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Enhance your understanding of the Bohr atom, modelled as a wave or as a particle, by referring to your Electronic Learning Partner.

The Quantum Mechanical Atom

Bohr's model of the atom very successfully explained many of the confusing properties of the atom — it marked a monumental first step into the quantum nature of the atom. Nevertheless, the model was incomplete. For example, a very precise examination of the spectrum of hydrogen showed that what had at first appeared to be individual lines in the spectrum were actually several lines that were extremely close together. As illustrated in Figure 12.21, this “fine structure,” as it is sometimes called, could best be explained if one or more energy levels was broken up into several very closely spaced energy levels.

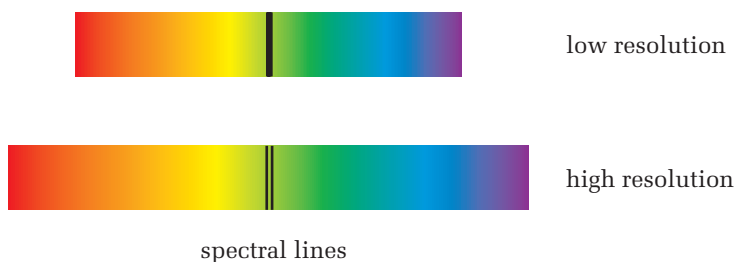


Figure 12.21 Very close examination of the lines in the hydrogen spectrum showed that some of the lines were made up of several fine lines that were very close together.

Another feature of emission spectra that the Bohr atom could not explain was observed in 1896 by Dutch physicist Pieter Zeeman (1865–1943). He placed a sodium flame in a strong magnetic field and then examined the emission spectrum of the flame with a very fine diffraction grating. He observed that the magnetic field caused certain spectral lines to “split” — what had been one line in the spectrum became two or more lines when a magnetic

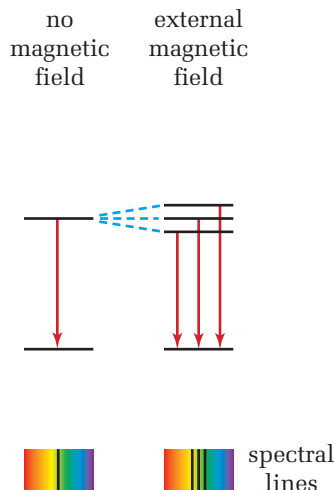


Figure 12.22 When a sample is placed in a magnetic field, some individual spectral lines become a set of closely spaced lines.

field was present. This phenomenon, illustrated in Figure 12.22, is now called the **Zeeman effect**.

Several physicists attempted with some success to modify the Bohr model to account for the fine structure and the Zeeman effect. The greatest success, however, came from an entirely different approach to modelling the atom: De Broglie's concept of matter waves paved the way to the new quantum mechanics or, as it is often called, "wave mechanics."

When de Broglie proposed his hypothesis about matter waves (about 10 years after Bohr had developed his model of the atom), he applied the ideas to the Bohr model. De Broglie suggested that when electrons were moving in circular orbits around the nucleus, the associated "pilot waves," as de Broglie named them, must form standing waves. Otherwise, destructive interference would eliminate the waves. To form a standing wave on a circular path, the length of the path would have to be an integral number of wavelengths, as shown in Figure 12.23. The procedure that follows the illustration will guide you through the first few steps of de Broglie's method for determining the radius of the orbit of the electron matter waves around the nucleus.

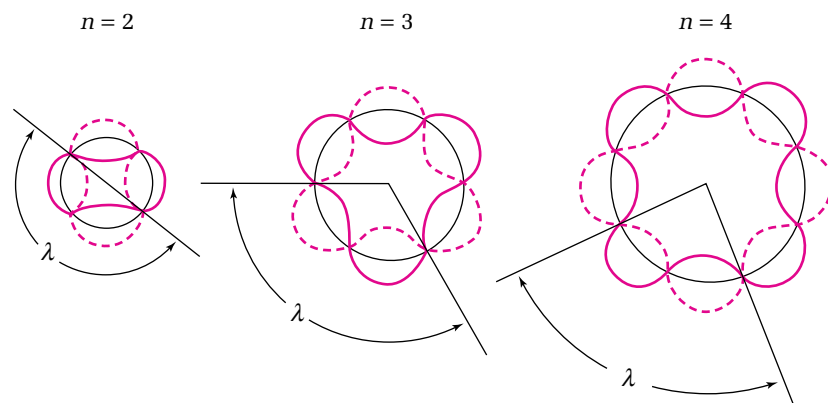


Figure 12.23 The number of wavelengths of matter waves that lie on the radius of an electron orbit is equal to the value of n for that energy level. No other wavelengths are allowed because they would interfere destructively with themselves.

- Write the formula for the circumference of a circle and set it equal to any integer (n) times the wavelength.
- Write de Broglie's formula for the wavelength of a matter wave.
- Substitute de Broglie's wavelength of an electron into the first equation.
- Divide both sides of the equation by 2π .
- Multiply both sides of the equation by $m_e v_n$

$$2\pi r_n = n\lambda, \text{ where } n = 1, 2, 3, \dots$$

$$\lambda = \frac{h}{mv}$$

$$2\pi r_n = n \frac{h}{m_e v_n}$$

$$r_n = \frac{nh}{2\pi m_e v_n}$$

$$m_e v_n r_n = \frac{nh}{2\pi}$$

Notice that the last equation is the same as Bohr's expression for the quantization of angular momentum. From this point on, the derivation of the equation for the radius of allowed orbits would be exactly the same as Bohr's derivation. Using two entirely different approaches to the quantization of electron orbits, Bohr's and de Broglie's results were identical.

In 1925, Viennese physicist Erwin Schrödinger (1887–1961) read de Broglie's thesis with fascination. Within a matter of weeks, Schrödinger had developed a very complex mathematical equation that can be solved to produce detailed information about matter waves and the atom. The now-famous equation, called the **Schrödinger wave equation**, forms the foundation of quantum mechanics. When you insert data describing the potential energy of an electron or electrons in an atom into the wave equation and solve the equation, you obtain mathematical expressions called “wave functions.” These **wave functions**, represented by the Greek letter ψ (psi), provide information about the allowed orbits and energy levels of electrons in the atom.

Wave functions account for most of the details of the hydrogen spectra that the original Bohr model could not explain. However, Schrödinger's wave functions could not predict one small, magnetic “splitting” of energy levels. British physicist Paul Adrien Maurice Dirac (1902–1984) realized that electrons travelling in the lower orbits in an atom would be travelling at excessively high speeds, high enough to exhibit relativistic effects. In 1928, Dirac modified Schrödinger's equation to account for relativistic effects. The equation could then account for all observed properties of electrons in atomic orbits. In addition, it predicted many phenomena that had not yet been discovered when the equation was developed.

You are probably wondering, “What are wave functions and what do the amplitude and velocity of a matter wave describe?” Many physicists in the early 1900s asked the same question.

Wave functions do not describe such properties as the changing pressure of air in a sound wave or the changing electric field strength in an electromagnetic wave. In fact, wave functions cannot describe any real property, because they contain the imaginary number i ($i = \sqrt{-1}$, which does not exist). You must carry out a mathematical operation on the wave functions to eliminate the imaginary number in order to describe anything real about the atom.

The result of this operation, symbolized $\psi^*\psi$, represents the probability that the electron will occupy a certain position in the atom at a certain time. You could call the wave function a “wave of probability.” You can no longer think of the electron as a solid particle that is moving in a specific path around the nucleus of an atom, but rather must try to envision a cloud such as the one shown in Figure 12.24 (A) and interpret the density of the cloud as the probability that the electron is in that location. These “regions

COURSE CHALLENGE

Waves and Particles

The process of science continues to discover truths about the nature of our universe. How far have we really come? How well are we able to describe our world? Refer to page 605 for ideas to help you incorporate philosophical debate into your *Course Challenge*.

PHYSICS FILE

Solutions to Dirac's modification of the Schrödinger wave equation predicted twice as many particles as were known to exist in the systems for which the equation was defined. Dirac realized that one stage in the solution contained a square root that yielded both positive and negative values. For example, $\sqrt{16y^4} = \pm 4y^2$. You have probably solved problems involving projectile motion or some other form of motion and found both positive and negative values for time. You simply said that a negative time had no meaning and you chose the positive value. Dirac tried this approach, but it changed the final results. Dirac's original results seemed erroneous because they predicted the existence of antiparticles, which had not yet been discovered. Soon after, antiparticles were observed experimentally by other scientists. You will learn about antiparticles in Chapter 13, *The Nucleus and Elementary Particles*.

in space” occupied by an electron are often called **orbitals**. If the orbital of the electron is pictured as solid in appearance, as shown in Figure 12.24 (B), it means that there is a 95% probability that the electron is within the enclosed space.

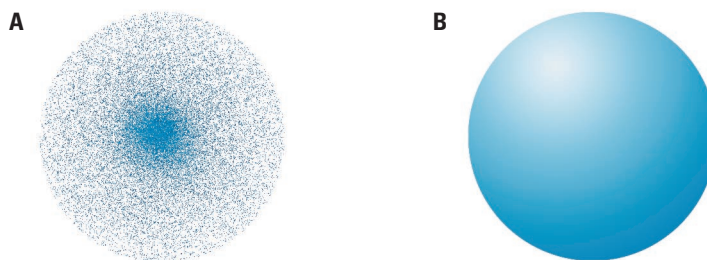


Figure 12.24 When you plot $\psi^*\psi$, you obtain orbitals such as these. **(A)** Orbitals drawn in this manner show the probability of finding the electron. **(B)** Often orbitals are drawn with solid outlines. The probability that the electron is within the enclosed space is 95%.

You might also wonder if the Bohr model was wrong and should be discarded. The answer to that question is a resounding no. The wave functions — that is, the solutions to the Schrödinger wave equation — give the same energy levels and the same principal quantum number (n) that the Bohr model gave. Also, the distance from the nucleus for which the probability of finding the electron is greatest is exactly the same as the Bohr radius. These results show that the general features of the Bohr model are correct and that it is a very useful model for general properties of the atom. The wave equation is necessary only in the finer details of structure.

Quantum Numbers

The wave functions obtained from Schrödinger’s wave equation include two more quantum numbers in addition to the principal quantum number, n . Dirac’s relativistic modification of the Schrödinger equation adds another quantum number, making a total of four quantum numbers that specify the characteristics of each electron in an atom. Each quantum number represents one property of the electron that is quantized.

The principal quantum number, n , represents exactly the same property of the atom in both the Bohr model and the Schrödinger model and specifies the energy level of the electron. The value of n can be any positive integer: 1, 2, 3, 4, These energy levels are sometimes referred to as “shells.”

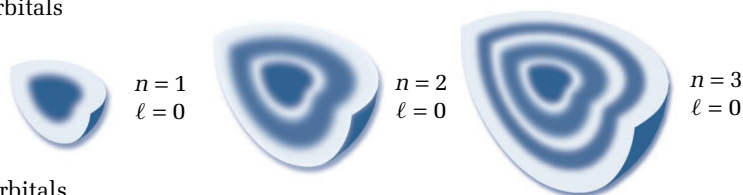
The **orbital quantum number**, ℓ , specifies the shape of the orbital. The value of ℓ can be any non-negative integer less than n . For example, when $n = 1$, $\ell = 0$. When $n = 2$, ℓ can be 0 or 1. In chemistry, orbitals with different values of ℓ (0, 1, 2, 3, ...) are assigned the letters s , p , d , f , Figure 12.25 shows the shapes of orbitals for the first three values of ℓ .

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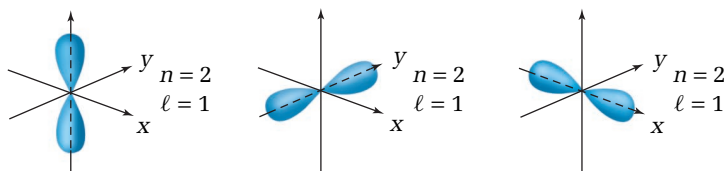


Your Electronic Learning Partner contains an excellent reference source of emission and absorption spectra for every element in the periodic table.

s orbitals



p orbitals



d orbitals

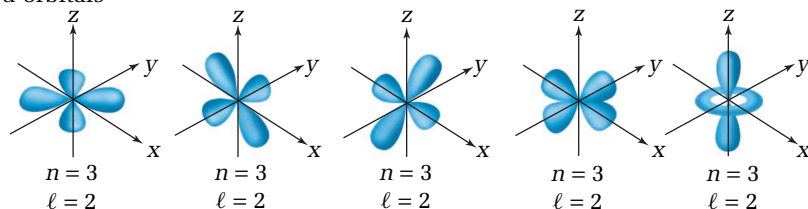


Figure 12.25 Orbitals for which $\ell = 0$ (s orbitals) are always spherical. When $\ell = 1$ (p orbitals), each orbital has two lobes. Four of the $\ell = 2$ (d) orbitals have four lobes and the fifth $\ell = 2$ orbital has two lobes plus a disk.

The orbital quantum number is sometimes called the “angular momentum quantum number,” because it determines the angular momentum of the electron. If an electron was to move along a curved path, it would have angular momentum. Although it is not accurate to think of the electron as a tiny, solid piece of matter orbiting around the nucleus, some properties of the electron clouds of orbitals with ℓ greater than zero give angular momentum to the electron cloud. Electrons that have the same value of n but have different values of ℓ possess slightly different energies. As illustrated in Figure 12.26, these closely spaced energy levels account for the fine structure in an emission spectrum of the element.

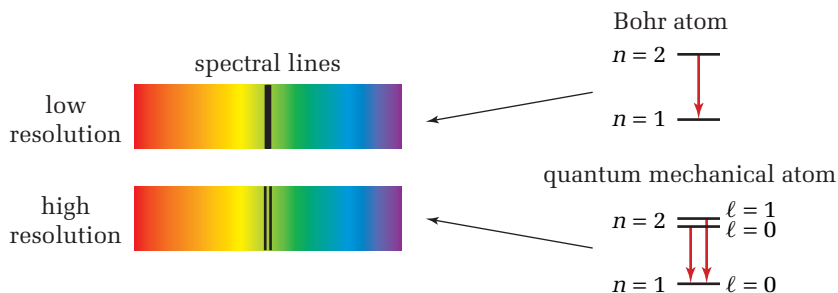


Figure 12.26 For any energy level (shell) for which $n > 0$, there is more than one value of the orbital quantum number, ℓ . The orbitals for each value of ℓ have slightly different energies. These closely spaced energies account for the fine structure, that is, the presence of more than one spectral line very close together.

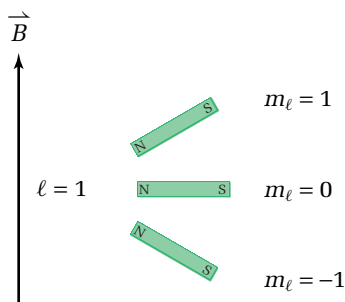


Figure 12.27 In the absence of an external magnetic field, the ℓ orbitals can take any random orientation in space. When a sample is placed in a magnetic field, the ℓ orbitals take on specific orientations in relation to the external field.

The **magnetic quantum number**, m_ℓ , determines the orientation of the orbitals when the atom is placed in an external magnetic field. To develop a sense of what this quantum number means, it is once again helpful, although not entirely accurate, to think of the electron in its cloud as an electric current flowing around the nucleus. As you know, a current flowing in a loop creates a magnetic field. The magnetic quantum number determines how this internal field is oriented if the atom is placed in an external magnetic field. In Figure 12.27, the electron's magnetic field is represented by a small bar magnet with different orientations in an external magnetic field.

The **spin quantum number**, m_s , results from the relativistic form of the wave equation. The term “spin” is used because the effect is the same as it would be if the electron was a spherical charged object that was spinning. A spinning charge creates its own magnetic field in much the same way that a circular current does. The value of m_s can be only $+\frac{1}{2}$ or $-\frac{1}{2}$. Similar to the magnetic quantum number, the spin quantum number has an effect on the energy of the electron only when the atom is placed in an external magnetic field. The two orientations in the external magnetic field are often called “spin up” and “spin down.” Figure 12.28 illustrates the two possible orientations of the electron spin and its effect on the electron's energy and spectrum in an external magnetic field.

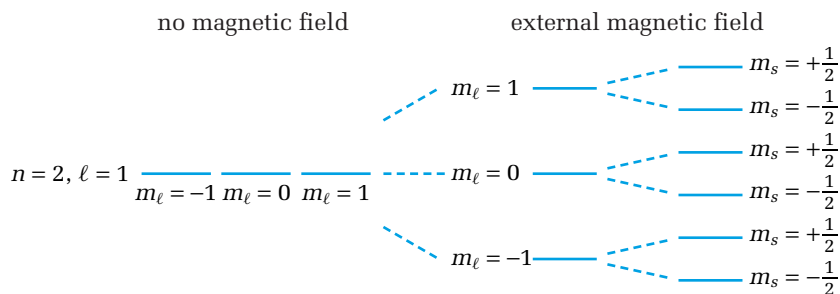


Figure 12.28 The electron spin can assume any orientation in the absence of an external magnetic field, but can take only two orientations when placed in a magnetic field — spin up or spin down.

These four quantum numbers and the associated wave functions can explain and predict essentially all of the observed characteristics of atoms. Two questions might arise, however: If almost all of the mass of an atom is confined to a very tiny nucleus and electrons, with very little mass, are in “clouds” that are enormous compared to the nucleus, why does matter seem so “solid”? Why cannot atoms be compressed into much smaller volumes?

Austrian physicist Wolfgang Pauli (1900–1958) answered those questions in 1925. According to the **Pauli exclusion principle**, *no two electrons in the same atom can occupy the same state*. An easier way of saying the same thing is that *no two electrons in the same atom can have the same four quantum numbers*. Electron clouds of atoms cannot overlap.

The Pauli exclusion principle also tells us how many electrons can fit into each energy level of an atom. The tree diagrams in Figure 12.29 show how many electrons can fit into the first three energy levels, $n = 1$, $n = 2$, and $n = 3$.

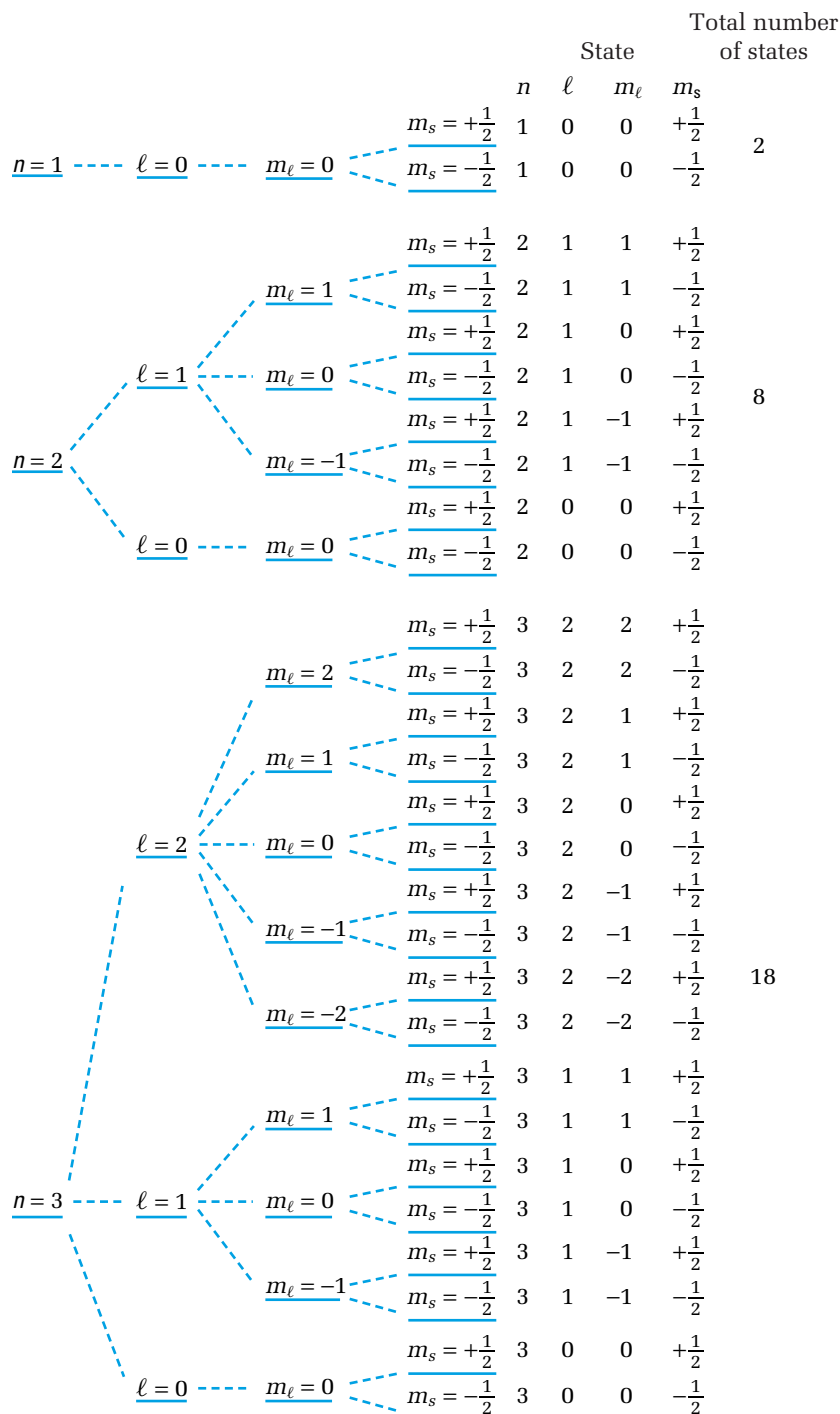
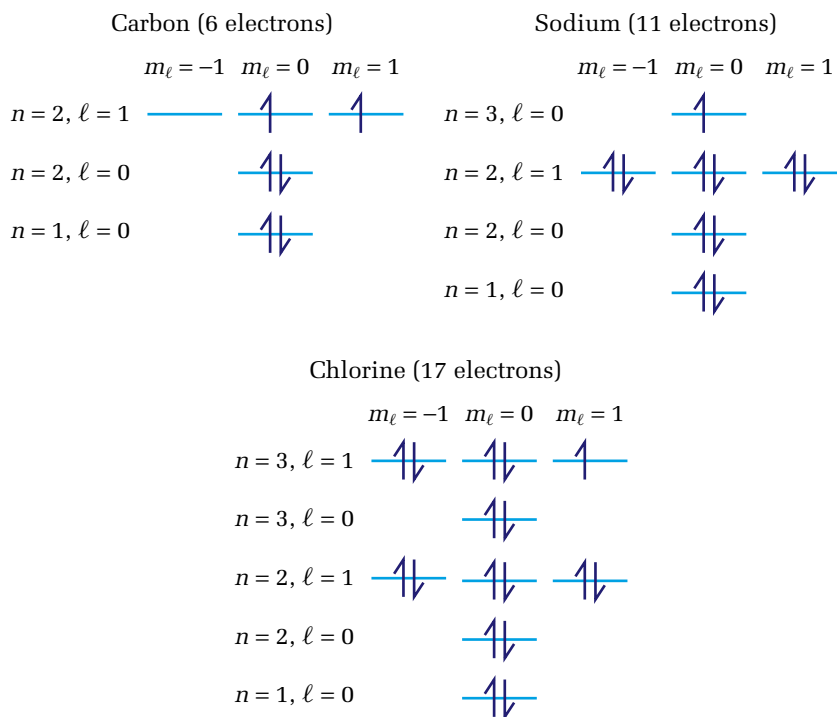


Figure 12.29 These tree diagrams show the energy levels, both in the absence and the presence of an external magnetic field, for the first three values of the principal quantum number, n .

• Conceptual Problem

- Study Figure 12.29 and then draw a tree diagram for the next energy level, $n = 4$. How many electrons will fit into the fourth energy level?

Hydrogen has only one proton in the nucleus, and thus one electron in an orbital. When a hydrogen atom is not excited, the electron is in the $n = 1, \ell = 0$ energy level. However, the atom can absorb energy and become excited and the electron can “jump” up to any allowed orbital. All elements other than hydrogen have more than one electron. When atoms are not excited, the electrons are in the lowest possible energy levels that do not conflict with the Pauli exclusion principle. Figure 12.30 gives examples of three different elements with their electrons in the lowest possible energy levels. This condition is called the **ground state** of the atom. Similar to the electron in hydrogen, the electrons of other elements can absorb energy and rise to higher energy levels.



↑ electron with spin up ($m_s = +\frac{1}{2}$)

↓ electron with spin down ($m_s = -\frac{1}{2}$)

Figure 12.30 Electrons “fill” the energy levels from the lowest upward until there are as many electrons in orbitals as there are protons in the nucleus.